

Resonant, Core Level and Angle Resolved Photoemission Studies of Rare Earth Hexaborides

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INTRODUCTION

The traditional understanding [1,2,3] of the electronic structure of the cubic compounds AB_6 where A is Sr or a rare earth is that a boron-based valence band is separated by a gap from an A-based conduction band. The boron bonding is such that the valence band lacks two electrons per formula unit of being filled. Whether the material is an insulator or a metal then depends simply on the valence of A, under the reasonable assumption that the partially filled 4f shell of a rare earth element will not lead to conductivity. In this view, SrB_6 with divalent Sr is a normal band insulator, ferromagnetic EuB_6 has divalent Eu and is an insulator, LaB_6 is a metal with trivalent La giving one electron to the La based conduction band, and SmB_6 with Sm mixed valent between divalent and trivalent should also be a metal. With the exception of trivalent metals like LaB_6 [4], this simple view has proved remarkably difficult to establish. Hints of non-insulating behavior in EuB_6 have been ascribed to non-stoichiometry [5] or have caused speculations that EuB_6 is mixed valent [5] or a semi-metal [6]. Various properties of SmB_6 force the view, initially controversial [7] but then established [8], that it has a small single-particle gap, of order 5 to 10 meV, at E_F . However, the situation is further complicated by more recent findings on SmB_6 which imply states within this gap on yet a lower energy scale [9].

Of a group of small-gap mixed valent materials [10-12], SmB_6 was the first to be clearly identified [8]. The earliest picture [13] of the formation of the energy gap was that of a very narrow f-level crossing a broad conduction band just at E_F so that a gap can be opened by f-conduction band hybridization. Such a picture can be explicitly constructed [14] and linked [15] to the Luttinger theorem by interpreting the f-band as the lowest lying fermion excitation of the $f^6 \rightarrow f^5$ type, and by a symmetry analysis showing that, for SmB_6 at least, such a gap can indeed be opened everywhere in the Brillouin zone. A more recent view of these materials, leading to the name “Kondo insulators” replaces the narrow f-level by the effective f-level associated with the Kondo resonance [16,17,18]. Although the Kondo view appears to work well for Ce materials such as $Ce_3Bi_4Pt_3$ [19], which are known to be in the Kondo regime of the Anderson model, it is quite unclear that this view applies to SmB_6 , which is strongly mixed valent and displays $f^6 \rightarrow f^5$ transitions just at E_F within experimental resolution.

We have performed complementary photoemission studies at the ALS and the Wisconsin Synchrotron Radiation Center (SRC), in a continuing program directed at the various issues described above. Results to date are described in this abstract.

SrB_6 and EuB_6

Traditionally it has been regarded as important to study the electronic structure of single valent materials such as SrB_6 , LaB_6 and EuB_6 as reference materials for the more complex problem of the mixed valence of SmB_6 . However, efforts to verify the traditional view of the hexaboride band structure in SrB_6 and EuB_6 have yielded surprises. Band calculations [20,21] show the possibility

that both materials could be intrinsic semimetals due to a small overlap of the valence and conduction bands at the X-point, and recent transport [22,23,24] and Shubnikov-de Haas data [24] require either this semi-metal possibility or off-stoichiometry for SrB_6 , or additionally for EuB_6 , that it is slightly mixed valent.

Early studies [25] of the Eu 4f spectrum of EuB_6 left open the possibility of slight Eu mixed valence, either intrinsic or due to off-stoichiometry. We have eliminated this possibility by careful resonant photoemission studies at the ALS. Fig. 1 shows the strong enhancement of the $\text{Eu}^{2+} 4f^7 \rightarrow 4f^6$ emission at binding energy $E_B \approx 1\text{ eV}$ as the photon energy is varied through the Eu $4d \rightarrow 4f$ absorption edge. No trace of $\text{Eu}^{3+} 4f^6 \rightarrow 4f^5$ emission, which would be displaced to higher E_B by the 4f Coulomb repulsion, can be seen.

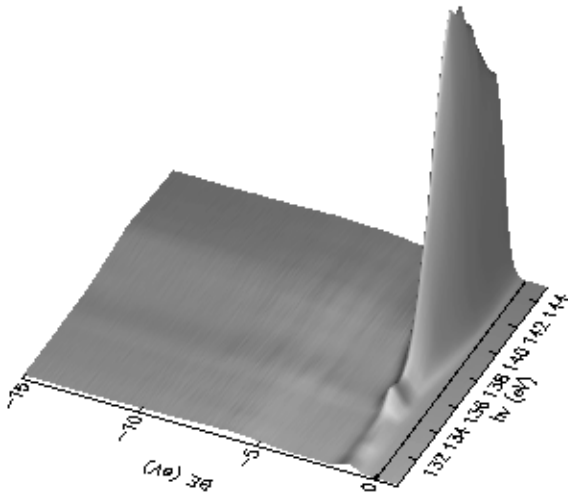


Figure 1. Resonant photoemission of EuB_6 at the Eu $4d \rightarrow 4f$ absorption edge. Only the $\text{Eu} 4f^7 \rightarrow 4f^6$ transition corresponding to divalent Eu is resonantly enhanced.

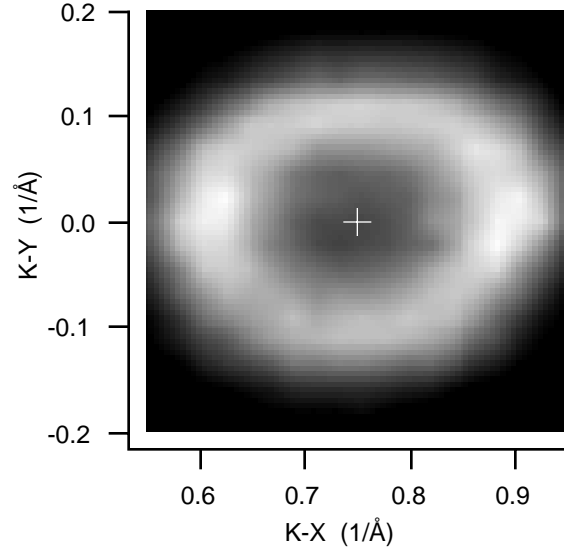


Figure 2. EuB_6 Fermi energy intensity map at $h\nu=30\text{ eV}$ centered around the X-point (+). The ring of bright intensity corresponds to a small electron pocket.

Angle resolved photoemission spectroscopy (ARPES) performed with low photon energies at the SRC provides strong evidence that both materials are semi-metals, through the finding of a small piece of Fermi surface (FS) around the X-point. The Fermi energy ARPES intensity map of Fig. 2 provides an image of the EuB_6 FS in the plane of the sample surface. The SrB_6 FS similar but much smaller, consistent with band theory. For EuB_6 the presence of a true FS has important implications [23] for understanding the exchange interactions leading to its ferromagnetism, and for SrB_6 this result provides a concrete framework in which to consider novel low temperature transport properties [22]. We are now analyzing these data and comparing to other evidence [22,23,24] concerning the carrier densities and FS sizes. Important implications for future studies are described below.

SmB_6

Early [26,27] photoemission and resonance photoemission studies of SmB_6 observed bulk $\text{Sm}^{2+} 4f^6 \rightarrow 4f^5$ emission just at E_F , within the experimental resolution, bulk $\text{Sm}^{3+} 4f^5 \rightarrow 4f^4$ emission at $E_B \approx 7\text{ eV}$, and $\text{Sm}^{2+} 4f^6 \rightarrow 4f^5$ emission surface-shifted by $\approx 0.6\text{ eV}$. Although our ALS resonant photoemission studies of cleaved single crystals do not have resolution adequate to observe the small gap expected at E_F , they have nonetheless revealed $4f^6 \rightarrow 4f^5$ structure additional to what was seen in early work. Fig. 3 shows the overall resonant structure and Fig. 4 shows the $4f^6 \rightarrow 4f^5$ spectrum at normal emission for a photon energy 135 eV just above the Sm $4d \rightarrow 4f$ edge.

Expected [28] atomic $4f^5$ final state structure is shown by the line spectrum. The splitting in the peak at $E_B \approx 3\text{eV}$ was not observed before. The peak nearest E_F shows three pieces of structure where only two are expected. The extra splitting cannot plausibly be ascribed to a surface shift, because the known surface shifted peaks give a replica $4f^5$ spectrum beginning at $E_B \approx 0.6\text{eV}$, and are not even seen in this normal emission spectrum. Further, crystal field splittings of the f^5 multiplets are generally not expected to exceed 10meV . Detailed and higher resolution studies of the near E_F feature are planned.

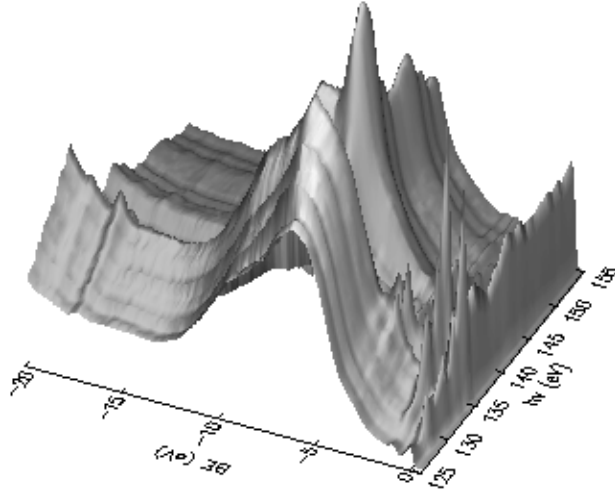


Figure 3. Resonant photoemission of SmB_6 at the Sm $4d \rightarrow 4f$ absorption edge. Both trivalent and divalent Sm resonant enhancements are present.

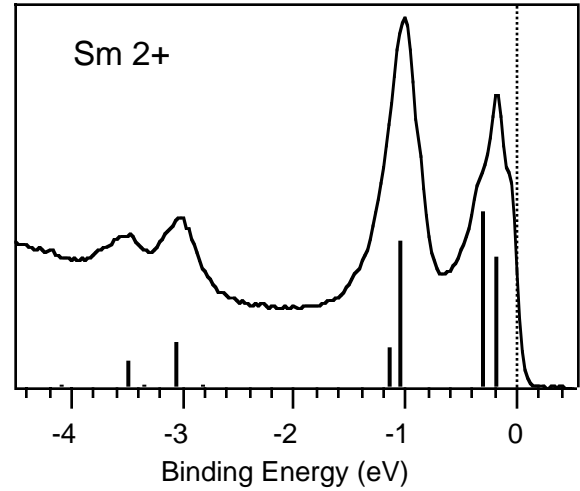


Figure 4. Sm $4f^6 \rightarrow 4f^5$ spectrum at the strongest Sm $2+$ resonance (135eV). Vertical bars are calculated final state multiplets.

The presence of strong $4f$ emission just at E_F has precluded directly imaging the non- $4f$ FS, but we have observed in ARPES spectra obtained at the SRC a dispersing peak which crosses E_F at essentially the k -value expected from band calculations [29] for LaB_6 , assuming the 0.6 conduction electrons/Sm implied by the Sm valence of 2.6 .

$\text{Sm}_{1-x-y}\text{Sr}_x\text{La}_y\text{B}_6$ Hexaboride Alloys

Our hexaboride compound results have motivated us to begin studying the alloy system $\text{Sm}_{1-x-y}\text{Sr}_x\text{La}_y\text{B}_6$. The general thrust of these studies is to address the relation between single ion and lattice mixed valence behavior, especially the possibility suggested by Haldane [30,31] that conduction electron screening can promote single-ion mixed valence by pinning the f -level to E_F . In the simplest model, without screening effects, the Sm $f^6 \leftrightarrow f^5$ energy is fixed relative to the conduction band. By varying x and y we can sweep E_F through this energy and so vary from Sm^{3+} in SrB_6 to Sm^{2+} in LaB_6 , and we can vary the concentration of Sm from concentrated to dilute while maintaining fixed the number of conduction electrons and hence E_F and hence, perhaps, the intermediate Sm valence. We can determine if the simple scenario actually occurs or if there is a tendency for the f -level to jump to E_F , or cling to E_F ,

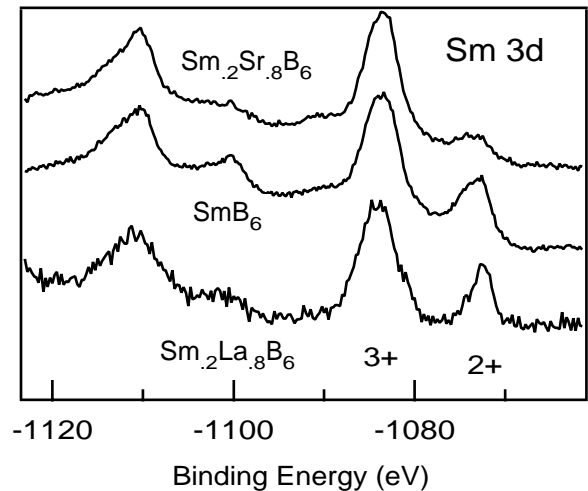


Figure 5. Sm $3d$ core level spectra using Al $K\alpha$ x-rays showing varying ratios of Sm $2+$ and Sm $3+$.

due to screening or to Sm-Sm interaction effects. The spectroscopic results will be correlated with transport studies done by M.C. Aronson. Preliminary studies of Sm core level spectra (see Fig. 5) to determine the valence in several alloy samples indicate departures from the simple scenario.

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